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A New Class of Double-Bridged Coordination
Polymers Based On Chromium(III)

by

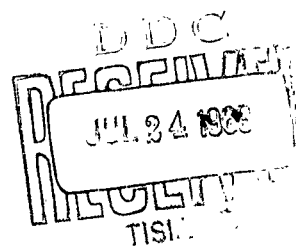
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PENNSALT CHEMICALS CORPORATION
Research and Development Department
Wyndmoor, Pennsylvania

June 1963

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A New Class of Double-Bridged Coordination Polymers Based on Chromium(III)

Sir:

Earlier reports from this laboratory have concerned the preparation of coordination polymers of types which we write symbolically as $[M(AB)X_2]_n$ ⁽¹⁾ and $[MX_2]_n$ ⁽²⁾ where AB represents a uninegative bidentate ligand and X repre-

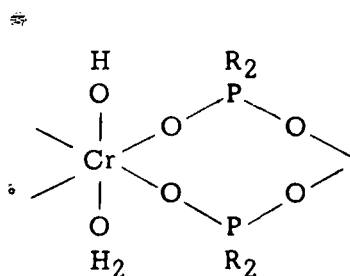
1. B.P. Block, J. Simkin, and L.R. Ocone, J. Am. Chem. Soc. 84, 1749 (1962).
 2. B.P. Block, S.H. Rose, C.W. Schaumann, E.S. Roth, and J. Simkin, Ibid. 3200.
-

sents a uninegative bridging group. We now wish to report a third class, $[M(a)(b)X_2]_n$, where a represents a neutral unidentate ligand and b a uninegative ligand. The preparation of this new class differs in method from that in the earlier series and appears to lead to polymers with substantially higher molecular weight than we have found for the other two types. The non-bridging ligands a and b are inorganic, so that this material is an example of a coordination polymer which in addition to its inorganic backbone has inorganic blocking groups in the repeating unit.

The synthesis is a two-step process in which chromium(II) acetate is treated with a potassium phosphinate ($KOPR_2O$) to yield the corresponding chromium(II) phosphinate ($R=C_6H_5$, I). The latter is then oxidized with air in the presence of water to yield the composition $Cr(H_2O)(OH)(OPR_2O)_2$ ($R=C_6H_5$, II) which has polymeric properties. II has been prepared by these reactions under a variety of conditions, but here we will only describe a set of conditions which gives a product exhibiting a high intrinsic viscosity in chloroform.

A suspension of 2.7 g. of freshly prepared $\text{Cr}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in 125 ml. of deoxygenated water is refluxed under nitrogen with stirring for 1 hr. After the addition of a deoxygenated solution of $\text{KOP}(\text{C}_6\text{H}_5)_2\text{O}$ (prepared by the exact neutralization of 8.0 g. of $(\text{C}_6\text{H}_5)_2\text{P}(\text{O})\text{OH}$ with 1 M. KOH) without exposure to air, the refluxing is continued for 2-3 hr. under nitrogen. The precipitated intermediate I is then separated by filtration at room temperature and washed several times with deoxygenated water, all operations being conducted under nitrogen. I is next dispersed in 500 ml. of water and oxidized to II by exposure to the atmosphere. After crude II has been removed by filtration, washed thoroughly with water, and dried at 100° , it is dissolved in benzene. The resulting solution is then separated from the small quantity of benzene insolubles (less than 0.3 g.) by filtration and evaporated at room temperature in a stream of nitrogen to yield II. Final drying is at 120° . Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{CrO}_6\text{P}_2$: C, 55.25%; H, 4.43%; Cr, 10.0%; P, 11.88%. Found: C, 56.39%; H, 4.36%; Cr, 9.7%; P, 11.93%. Yields vary from 70 to 95%. The intrinsic viscosity of II prepared in this manner is 0.6 to 0.7 in chloroform. Less rigorously controlled conditions lead to polymers with intrinsic viscosities from 0.1 to 0.5. Even unfractionated samples with intrinsic viscosities in the range 0.12 to 0.20 have number average molecular weights greater than 10,000 as determined by ebulliometry and vapor pressure osmometry in chloroform. Consequently the higher-viscosity samples certainly have molecular weights of at least several tens of thousands.

Although any of the groups present in II could serve as bridging groups, the most probable structure contains a double-bridged backbone similar to that suggested for $\text{Cr}(\text{AcCHAc})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2$ ¹ except that a *cis* configuration is not required. The infrared spectrum of II contains absorption peaks characteristic of PO_2 stretching with virtually the same frequency and absorption profile as found for polymeric $\text{Cr}(\text{AcCHAc})(\text{OP}(\text{C}_6\text{H}_5)_2\text{O})_2$ ¹. This is strong evidence that the diphenylphosphinate anion is functioning in the same way in both polymers. Furthermore, the hydroxyl group and the water O-H stretching vibrations can be identified separately at frequencies which suggest they are normally coordinated groups. Thus infrared indicates that the hydroxyl groups are not bridging groups. The solubility of II in benzene or chloroform accompanied by marked swelling and the high intrinsic viscosity values are good evidence for the presence of linear chains as the predominating species with cross-linking only of minor importance. The indications are, then, that the repeat unit is



Thermogravimetric analysis of II shows initial weight loss at 375° with a step in the 410-430° region which corresponds to a 3-10% weight loss. No

polymer melt temperature has been observed up to or well beyond the decomposition point. Surprisingly the polymer shows remarkable resistance to hydrolysis and other chemical degradation. For example, no change in intrinsic viscosity is observed upon refluxing a suspension of the polymer in water for several hours. A cast film of high-viscosity II plasticized with 30% Aroclor 1254 has a tensile strength of over 1900 p.s.i.

In addition to the diphenyl species described here we have also been able to prepare the analogues with phenylmethylphosphinate, dimethylphosphinate, and cacodylate bridging groups. The mechanism by which this kind of polymer forms is not clear. It would appear that the intermediate I could be a polymer somewhat analogous to the phosphinate polymers involving zinc, beryllium, and cobalt². The oxidation step then may merely serve to increase the oxidation state of the chromium and introduce the additional ligands. Alternatively polymerization may be involved in the oxidation step.

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